

CEMENT AND LIME MANUFACTURE

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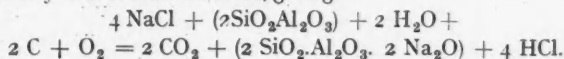
JANUARY, 1947

The Manufacture of Cement and Other Products.

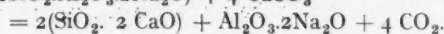
IN our number for September, 1946, we gave an abstract of a report published by H.M. Stationery Office describing the Séailles-Dyckerhoff process of extracting alumina from ashes, colliery waste, and similar material as practised in Germany. Owing to war-time conditions and other difficulties, it appears that the best results were not obtained from this process, and in the following we give a summary of a paper presented by Dr. J. C. Séailles at the Maison de la Chimie, Paris, in April, 1943. This paper describes Dr. Séailles's method and other methods for the production of alumina at cement works, and also the processes of obtaining other products in conjunction with the manufacture of cement. These products of associated manufacture are not by-products, but result from introducing selected materials into the cycle of cement production, whereby cement and other products of commercial value are obtained. Examples of associated manufacture, which have in some instances reached the stage of economic production, include: cement and alumina; cement and sulphuric acid; cement and iron; cement and phosphorus; cement, alumina, and sulphuric acid; cement, alumina, and iron; and cement, alumina, and phosphorus.

Alumina.

The principle of associating cement manufacture with that of alumina was suggested by Kayser in America in 1890, the process being to obtain Portland cement from the waste products of alumina manufacture. Kayser's initial process is based on two essential reactions: (i) Heating to above 1,100 deg. C. a mixture of clay and sodium chloride, giving



(ii) Re-heating in a kiln to about 1,400 deg. C. the sodium silico-aluminate thus obtained, ground with a calcareous substance to form sodium aluminate. This reaction is $(2\text{SiO}_2\text{Al}_2\text{O}_3 \cdot 2\text{Na}_2\text{O}) + 4 \text{ CaCO}_3$



(1)

B

The sodium aluminate extracted when filtered and treated by CO_2 produces alumina and sodium carbonate. The remaining dicalcium silicate, after adding suitable correctives, can be used for making Portland cement by heating in a kiln.

This process is theoretically attractive, since by using clay, sea-salt, and calcareous material it should be possible to obtain hydrochloric acid, alumina, sodium carbonate, and cement. There are, however, many practical difficulties, including in the first reaction the production of very impure hydrochloric acid at a high temperature, thus being a product of little value. The alumina obtained by CO_2 is also very impure and contains excess silica. The dicalcium silicate, rich in alkalis, is difficult to use for making cement. The only suitable product is the sodium carbonate. As a result of experiments over the past fifty years, some of these difficulties have been overcome.

The most recent form of this method is the Kayser-Cowles process. Briefly, the process comprises: (a) The additional production on a small scale of sodium silico-aluminate according to reaction (i) by heating to above 1,100 deg. C. a mixture of clay and sodium chloride, which results in the accessory production of HCl ; (b) Heating to about 1,400 deg. C. a mixture of clay, the sodium silico-aluminate derived from (a), limestone, and sodium aluminate; (c) Treatment of the heated product by extraction followed by precipitation; (d) Intensive washing of the residual sludge to eliminate the alkali; and (e) Reheating of the residual dicalcium silicate after adding the necessary correctives to obtain Portland cement. In this process HCl becomes a valueless residue, and is only produced to supply the cycle with the soda required to make up for losses. The disadvantages of this process include the use of concentrated sodium aluminate liquors, and consequently the sludge has to be subjected to considerable washing to obtain a residue that is sufficiently non-alkaline for use in cement manufacture. If high losses of soda are to be avoided, the washing water must be evaporated. There is also a loss of soda due to vaporisation in the kilns, and to the formation of sodium silico-aluminate in the course of extraction. The return of the spent sodium aluminate to the kiln and the already heated silico-aluminate entails additional heat treatment.

The Séailles-Dyckerhoff and Séailles-Ciments Français Processes.

These processes are the result of researches conducted since 1936 for the utilisation of silico-aluminous ores of all kinds, from siliceous bauxites to true clays. The process originally comprised: (i) Heating a mixture of silico-aluminous ore and limestone, so proportioned as to obtain a mixture of non-saturated aluminates of lime and dicalcium silicate; (ii) The solution in water of the non-saturated aluminates of lime, which are slightly soluble; no silica enters the solution; (iii) Precipitation of the aluminates of lime by CO_2 giving pure Al_2O_3 plus CaCO_3 ; (iv) Separation of Al_2O_3 and CaCO_3 ; and (v) Correction of the proportions of the residue and reheating to produce cement.

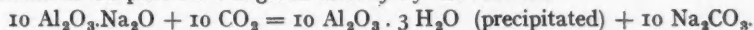
Improvements have made it possible to dispense with phase (iv) and to obtain pure alumina directly by dissolving the aluminate of lime in a very dilute liquor

of alkaline carbonates, possibly with other salts. The solution consists of sodium aluminate and calcium aluminate. If the operation is properly conducted no silica enters the solution, because the latter is insoluble in the presence of aluminate of lime. It is possible to obtain mixed solutions containing a preponderance of sodium aluminate, for example 90 per cent. of the latter and 10 per cent. of aluminate of lime.

If sodium carbonate is placed into a solution of this type, free from silica, the reaction is

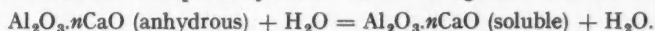


As the solution to be precipitated by CO_2 contains only pure sodium aluminate, alumina in the pure state is given directly by the reaction



Industrially, an appropriate fraction of Na_2CO_3 is merely reversed. The fraction of Na_2CO_3 used for precipitating CaCO_3 merely works in a closed circuit.

As the residual sludge retains extremely little alkali and may be used in cement manufacture, with washing limited to the quantity of water lost in the operations, no reconcentration is required. The alkali losses are negligible, in most cases being less than the amount of alkali supplied by the raw materials. The latter generally contain, after heating, enough soda and potash to maintain the charge. An additional recovery of alkali is even possible. For this process to be practicable it is essential to be able to manufacture by heating a substance containing aluminates of lime that are soluble in water and not only aluminates of lime that can be decomposed by soda. The following reaction must take place :



In other processes use is made of a double decomposition reaction, and as it is unnecessary for the calcium aluminate formed during the heat treatment to be soluble it may be of the type $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$, which sets in water without previous hydrolysis and consequently without passing into solution. The first firing is carried out under such conditions that a mixture of dicalcium silicate and anhydrous silicates of lime, soluble in water, is discharged from the kiln. The crude slurry is preferably obtained by mixing with the limestone some carbonaceous schists or ash containing a high proportion of carbon or unburnt material. Thus the first firing consumes very little fuel beyond that furnished by the raw materials. The product leaving the kiln is self-pulverising to such a high degree of fineness that the aluminates are readily dissolved. The grains of the extraction residue are peculiar, being already very fine, but are further etched by the dissolving of some of their constituents. The material for burning to cement is therefore a product which, after correction by the addition of limestone, exhibits the properties : (a) The greater part of the lime in the paste being already decarbonated, it requires no further heat to decompose the carbonate ; (b) Practically the whole of the silica, iron, and alumina is in the slurry in a combined state ; (c) The fineness results not from mechanical means but from chemical pulverisation, which produces a much finer product ; (d) The fine grains have large contact surfaces owing to the etching which they undergo during extraction ; (e) The

composition of the slurry is not determined by the inherent nature of local raw materials, but may be modified within wide limits by a more or less intensive extraction of the alumina. It thus becomes possible economically to make hyper-siliceous cements without the difficulty otherwise experienced in increasing the silica content independently of the alumina content.

The process is accompanied by reduced firing costs. The fuel consumption is low by reason of the decarbonation process, and the firing temperature is lower owing to the ultra-fine nature of the residues. It is claimed that cement obtained from this process possesses strengths that are higher than ordinary Portland cement (see Fig. 1). They are rapid-hardening, shrinkage is low, and the amount

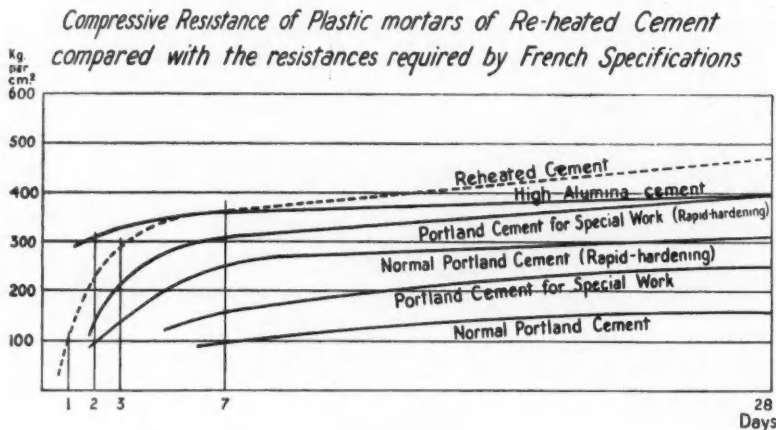


Fig. 1.

of heat generated during setting is relatively low. The explanation of these properties is partly that the reactions, being favoured by the degree of fineness, may be developed at from 600 deg. C. to 700 deg. C. The low CO_2 content of the atmosphere in the kiln is, moreover, not without effect.

Sulphuric Acid.

In our number for November, 1946, we described a process for the simultaneous manufacture of Portland cement and sulphuric acid. Dr. Séailles's paper briefly traces the development of the method from its inception by M. Basset in France about 1910 to the present works in Germany, England, and France. The basis of the process was described in our previous article.

The simultaneous manufacture of SO_2 and clinker entails the need for operating the furnace for two purposes, which is not without serious disadvantages, for the production of the clinker is itself a highly rigid operation incapable of being adapted to variations in composition of the fired product beyond very narrow

limits. Sulphate of lime (CaSO_4) may produce in the kiln, depending in part on the speed, either undecomposed CaSO_4 or CaS . In either case the operation proceeds as if the clinker were deficient in lime. It is necessary for the lime formed through the decomposition of the sulphate to combine completely with the other elements of the slurry. Variation in the speed of the kiln at the works at Miramas in France has been shown by M. Zorninger to give the following results:

Constituent.	Composition of clinker (per cent.)		
	Lower limit	Upper limit	Average
SO_3	0.5	2.0	1.65
S	0.0	0.8	0.30
SiO_2	19.0	22.0	20.21
R_2O_3	10.0	12.0	10.51
CaO	62.0	66.0	63.51
MgO	0.6	1.0	0.88
Free CaO	0.3	2.0	0.79

The average analysis with 0.3 per cent. sulphur, 1.65 per cent. SO_3 (that is, 2.75 per cent. CaSO_4) and 0.79 per cent. of free lime does not represent a good commercial clinker.

Iron.

M. Basset was apparently also the originator about 1929 of the idea of simultaneously producing Portland cement or hydraulic lime and iron or its carburised compounds, a process which has been tried in France. The principle is to fire, in a kiln, iron ore mixed with the elements of a Portland cement clinker, a procedure intended to produce a very pure iron due to the purifying action of a very basic slag. As this slag does not require to be melted, it can be rich in lime and therefore suitable for Portland cement.

During firing in a reducing medium, the ore is converted into metal and, while passing through the kiln, a genuine automatic puddling of the clinker is produced. The molten metal, exuded from the grains, collects and runs, while the slag is discharged as a non-molten clinker. The manufacture of iron by this process was soon found to be impracticable, but by using a more easily melted metal a more satisfactory method was obtained. Among the practical difficulties are the upkeep of the refractory material, the formation of rings in the furnace, and the regulation of the atmosphere in the kiln. Installations are at present in operation at Moncada in Spain and at Alhandra in Portugal.

The essential element is the rotary kiln of the type used in the cement industry, but the lining consists of two parts: that of the firing zone which consists of clinker bricks, and that of the rest of the furnace which is made of silico-aluminous bricks. To prevent the clinker from melting the firing zone is kept moist. In the event of adherence, mechanical rakes detach the rings. The kiln is fed by a dry homogeneous mixture of ore, carbonate of lime, and coal-dust. Heating by combustion of the coal-dust is regulated to maintain a reducing atmosphere.

The kiln is provided with a recess and a slot through which, at each revolution, the molten metal runs, while the clinker is discharged above the recess into a cooling drum. The metal produced is remarkably pure and uniform and the cement is of good quality. The real limitation of the Basset process is the necessity of treating only materials which make it possible to have an essentially silico-calcareous clinker, as excess alumina gives a product which does not comply with the definition of Portland cement. This difficulty is overcome by first accepting alumina in the slag and then by extracting it during the production of iron, alumina, and cement.

Alumina-Iron Cements.

A development of the foregoing process is the manufacture of alumina-iron cements. In experiments conducted by Dr. Séailles between 1930 and 1934 some almost white aluminates of lime were obtained in an electric furnace by reducing melting processes which gave iron or ferro-silicon as a by-product. Manufacture on these lines has been carried out near Hamburg using a blastfurnace. In Hungary, haematite iron and melted cement were obtained by the Gobbi-Just processes. The chief difficulty is that the aluminate of lime slag is only liquid above 1600 deg. C., and that it is difficult to obtain the required temperatures without using super-oxygenated air and without problems arising concerning the upkeep of the refractory material. The difficulties are not insoluble, and development is retarded mainly because the limited demand for the special type of cement produced makes the regular and remunerative sale of the slag impossible. The slag produced in this way may also be used as the raw material for extracting alumina, and these processes are in operation in Russia and elsewhere.

Phosphorus.

Proposals have been made for treating phosphates of lime in the presence of silica or alumina to obtain phosphorus or its derivatives and silicate of lime (which can be used like Portland cement), or aluminate of lime, which can be used as melted cement. These processes are not beyond the laboratory stage.

Triple Production.

Triple production has the advantage over double production of dividing the operations, thus making series production possible, so that in each stage only one commercial product has to be considered. In this respect the use of a transition product characterised by its solubility alone is of special interest. The following are the principal reasons: (i) When it is desired to manufacture directly a product such as cement average analyses do not mean very much, since a good average may result from the sum of defective products. When the product sought is characterised by its solubility, a good average is the only requirement. (ii) One of the difficulties in making cement is the fact that the quality is only known after tests that take several days. When a product is sufficiently characterised by its solubility and the properties of the solution obtained, the test only takes a few minutes. (iii) Cement tests are carried out on specimens weighing

about one kilogramme, while solubility tests are made on specimens of about one gramme ; a means is thus provided of readily detecting variations in quality.

The triple production of alumina, sulphuric acid and cement is obtained by the substitution of sulphate of lime for limestone in the processes already described, and necessary research work thereon is practically complete. The first firing merely decomposes the sulphate sufficiently. Experience has shown that, if the operation is carried out under favourable conditions, soluble aluminates are obtained without the undesirable formation of ternary elements.

The simultaneous production of alumina, iron and cement, which is easier and more profitable than the production of iron and cement only, was envisaged by Dr. Séailles in 1938. In the initial operation the mixture of soluble aluminates, dicalcium silicate, and molten metal can be obtained either by clinkerisation, similar to that used in the Basset processes, or by melting resulting in the formation of slag and metal. The clinker and the slag are self-pulverising, and the second operation consists of extracting the alumina. In a third stage the residue is corrected, and on reheating gives the hydraulic cement. The only difficulty is that of conducting the first operation under satisfactory conditions, and this operation differs little from that of M. Basset if the clinkerisation method is adopted. Indeed, the melting points are not very different between one case (tricalcium Portland clinker) and the other (bicalcium clinker). The melting process calls for a thorough study on account of the low fusibility of the slags obtained by comparison with the usual compositions. In this type of manufacture the use of schist or ash-containing unburnt fuel leads to some interesting possibilities.

In the production of alumina, phosphorus and cement the problems and their solutions are similar to the last case.

The economy of the processes described can be illustrated by the example of the triple production of alumina, sulphuric acid and cement according to the Séailles process. Starting with sulphate of lime and schists, the first heating process yields the SO_2 . This operation is not costly, owing to the amount of fuel supplied in the raw material being as much as 20 per cent. of the clinker produced. The heated product gives alumina by the extraction process described and on reheating the residue a cement possessing exceptional properties is obtained. The relative amounts of the various products are 1 ton of alumina, $6\frac{1}{2}$ tons of SO_2 , and 12 tons of cement.

The Manufacture of Building Plasters in France.

AN account of the methods of manufacture used in the plaster industry in France is given by M. Honoré Schmitt in "Revue des Matériaux de Construction et de Travaux Publics" for January, 1946. Some of these methods differ from those commonly used in Great Britain and the United States.

The author states that gypsum is found in many varieties in France, some deposits being free from foreign matter and giving the fine white plasters used for ornamental work. The most numerous and important deposits are of inferior quality and give plasters that are employed in more general work or are used as sulphate of lime for agricultural purposes. It is the treatment of the inferior materials that is considered in the following, wherein is examined the simplest

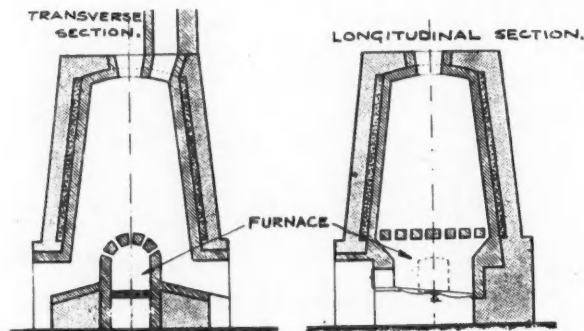


Fig. 1.—Vertical Kiln with Internal Furnace.

and most economical methods of manufacture. The low selling price of plaster does not permit expensive or complicated processes.

The chemical composition of gypsums are commonly as follows: Lime, 28 per cent. to 35 per cent.; sulphuric acid, 42 per cent. to 45 per cent.; water 30 per cent. to 20 per cent. They also contain mineral salts that affect the colour of the plaster, which may be green-grey, grey, blue-green, red, etc. Depending on the nature of the gypsum, the resulting plasters are of one of two types, namely, fine white plasters for moulding and surgical purposes or ordinary building plasters.

The object of the treatment is to free the stone of its water of crystallisation. This process is complex in practice, and the methods adopted in any factory have to take into account the characteristics of the gypsum available. Only in the past 20 years have the problems of the manufacture of plasters received attention from specialists, who have developed new methods and equipment which produce superior products. These new methods, however, introduce complications and additional costs.

In many old factories producing building plasters, crude types of vertical masonry kilns are still used. The furnace space is formed below an arch built from part of the material to be dehydrated. This arch supports the bulk of the gypsum with which the upper part of the kiln is completely filled and through which the hot gases percolate. To discharge the kiln the firebars are removed and the arch is broken, thereby causing the treated material to fall to the bottom of the kiln from which it is removed by an opening in one side. As this type of kiln works intermittently several kilns are necessary, but the first cost of each is low. They require considerable labour for their operation and, since the dehydrated material must be cooled before it can be removed from the kiln, the

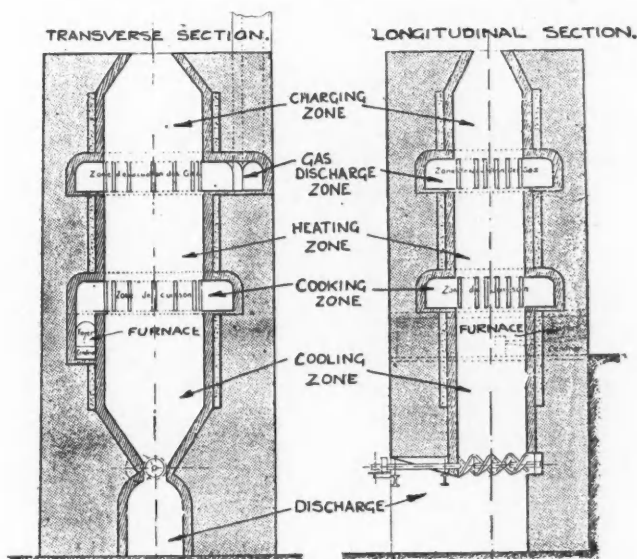


Fig. 2.—Continuous Vertical Kiln with External Furnace.

operation is slow. The quality of the product is variable, the material from the lower part of the kiln being over-treated and that from the upper under-treated. Thus, after removal from the kiln, all the material must be well mixed to obtain a product of uniform quality. The larger stones taken from the kiln exhibit the same variability, the outer parts of each stone being over-treated so that subsequent crushing and mixing are required.

The use of continuously operating vertical kilns (*Fig. 1*) with permanent interior furnaces obviates many of the disadvantages of the cruder type. The furnace-arch is constructed of refractory bricks, and perforations in the arch permit the hot gases to ascend through the material to a chimney in the roof of

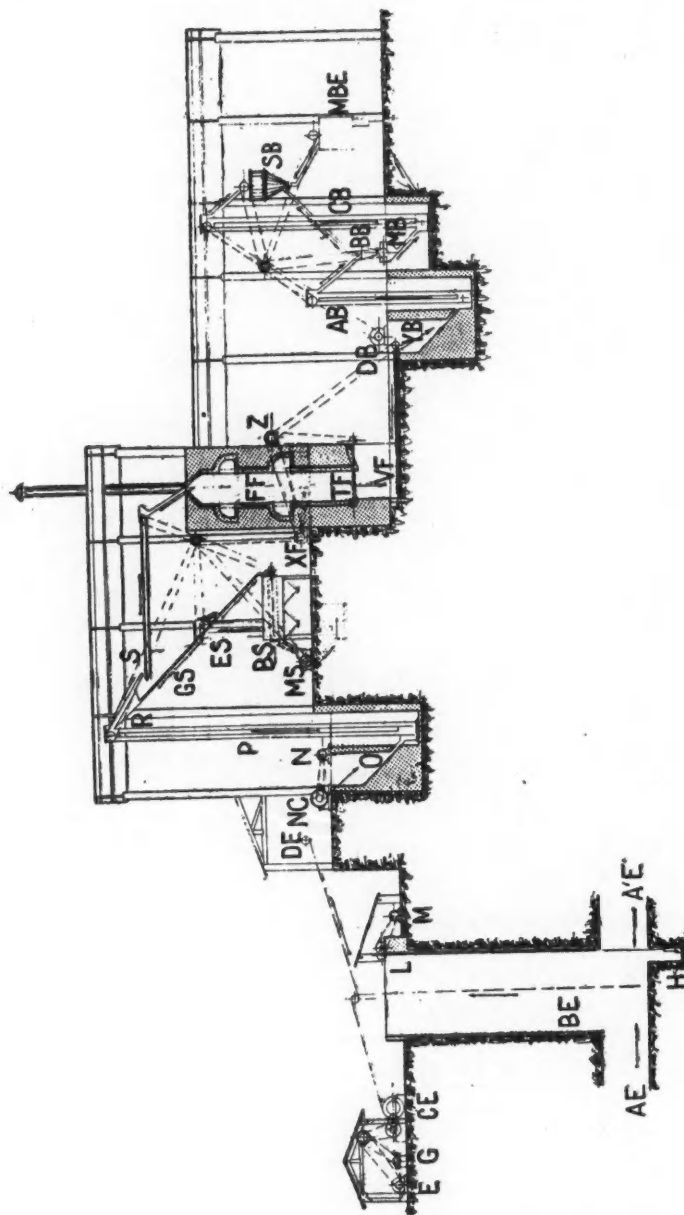


Fig. 3.—Arrangement of Plant at Factory for Manufacturing Plaster.

the kiln. The material is fed into the kiln through an opening in the roof, the opening being kept closed except when the kiln is being charged. The shape of the kiln is a hollow truncated cone with a refractory lining. Discharge is through doors at ground level in two opposite sides. The operation is continuous insofar as material fed in at the top gradually descends to the bottom as the material at the bottom is removed. There is a tendency for currents of hot gases to ascend directly from the furnace to the chimney, and as a result material in parts of the kiln remote from the path of the gases is under-treated. Moreover the material is discharged at a high temperature, and it is therefore necessary for it to be cooled in the open air before grinding. The fuel consumption in this form of kiln is lower than in the more primitive type and the rate of production is higher. The refractory bricks around the furnace quickly deteriorate.

To overcome the disadvantage of the kiln with the interior furnace, a continuously operating kiln with an external furnace (*Fig. 2*) was devised. The material is fed in at the top and in descending to the bottom of the kiln it passes through various zones. The upper zone contains the raw material. In the middle portion of the kiln is the heating zone, below which is the dehydrating zone. The furnace is in the wall of the kiln adjacent to the dehydrating zone and the hot gases enter the kiln through openings in an annular gallery in the walls at this level and pass upwards to escape to the chimney at a level immediately above the heating zone. Below the dehydrating zone is the cooling zone, at the bottom of which is the discharge opening. Discharge is by hand or mechanically by a screw conveyor that discharges directly into wagons; or the material may be transported to the grinding mills by a screw conveyor. Between the refractory lining of the kiln and the masonry walls there is an insulation space which is filled with sand. Although this type of kiln can deal with blocks of gypsum of any practicable size, it is preferable that all blocks are reduced to a size that will pass a ring of 2 in. diameter so that the dehydration of the interior of the particles is effected as well as that of the periphery.

An example of the arrangement of a plaster factory near Marseilles is shown in *Fig. 3*. The gypsum is extracted from the ground in the mine galleries at AE and A'E' and lifted to ground level up the shaft (BE) by the winch (CE). A conveyor transports the material into the factory at DE. The electric motor at E operates the winch and the compressor at G which supplies air for the pneumatic tools used in the mine. The pumping equipment at H, L, and M keeps the mine free from water.

The gypsum is fed by hand into a crusher (NC) which reduces the blocks to a size not exceeding 2 in., and the crushed material falls into the storage bin (O). An elevator (P) carries the crushed gypsum to the rotating screen (R), the mesh of which allows fines and all pieces below $\frac{3}{4}$ in. to pass down the chute (GS) to the plant below, where the material is prepared for use as fertiliser. The pieces exceeding $\frac{3}{4}$ in. in size are transported by the conveyor (S) to the kiln (FF), which is of a type similar to that shown in *Fig. 2*. The dehydrated material discharges at VF and is automatically transported to the bin (YB) from which, by means

of the elevator (AB) and the hopper (BB), it is transported to the grinding mill (MN). The ground material is passed to the air-separator (SB) which extracts the fine material and conducts it to the bagging machine (MBE). Material insufficiently ground is returned direct to the hopper (BB).

The minimum amount of labour required for the operation of this works includes an overseer for the mine, two miners, two men to load gypsum into the hoist, one man in charge of the motor, air-compressor, and pump, and one man operating the crusher; that is, six men are employed on the supply of gypsum to the factory. In the factory four men are required to maintain a daily output of 25 to 30 tons of plaster. These include the overseer, one man in charge of the fertiliser plant, one man in charge of the grinding, separating, and bagging plant, and one general labourer.

Expanding and Non-Shrinking Cements.

THE shrinkage that occurs upon the setting of pastes of most cements used in construction has lead to the need for a cement that does not exhibit this phenomenon, and for the solution of some engineering problems attention has been given to the production of a cement that expands upon setting. As was mentioned by Mr. H. B. Seed in our number for November, 1946, non-shrinking and expanding cements have been developed during the past twelve years by M. Henri Lossier, M.Soc.C.E.(France), in conjunction with cement manufacturers in France. An account of this development and of the practical applications of these special cements are given by M. Lossier in a paper entitled "Cements with Controlled Expansions and Their Applications to Prestressed Concrete," in the "Structural Engineer" for October, 1946, from which the following notes have been compiled.

Properties of Cements with Controlled Expansion.

The basis of an expanding cement is an ordinary artificial Portland cement with which is mixed a sulphoaluminate cement to act as an expanding agent. A stabilising agent, usually slag cement, is also necessary to stop the expansion when required by absorbing the principal reagent, the calcium sulphate. By adjusting the proportions of the constituents the amount and duration of the expansion can be accurately controlled, and regulation is possible during the time the cement is actually in use.

The amount of the linear expansion of a paste of neat cement may be as much as 0.05 of the initial length, and the time taken for this expansion may be regulated from a minimum of 24 hours to a maximum of over 30 days. In practice, however, such extremes are not required, and an expansion coefficient of 0.01 to 0.015 for the neat cement is sufficient. In some instances it is only necessary to have a paste that will not shrink, and the expansion of such a cement need only be sufficient to compensate for the shrinkage on drying. A non-shrinking neat cement has therefore a coefficient of expansion of 0.003 to 0.004.

The period during which expansion is generally allowed to operate is from ten to fifteen days. A greater rate of expansion results in the stresses, due to the external reaction that in practice operates against the internal expansive forces, being developed before the cement has attained sufficient compressive strength. A slower rate introduces practical difficulties, as the concrete must be kept sufficiently wet during the expansion period to maintain the expanding reactions.

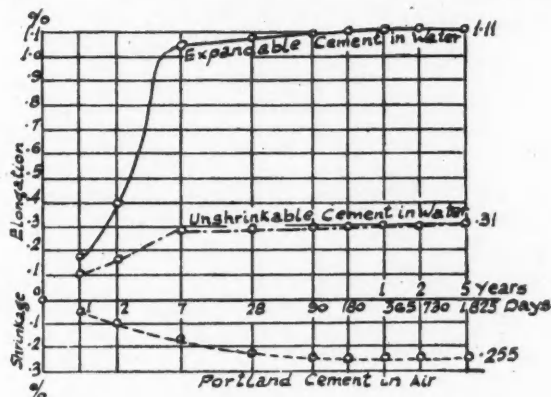


Fig. 1.—Expansion of Cement Cured in Water.

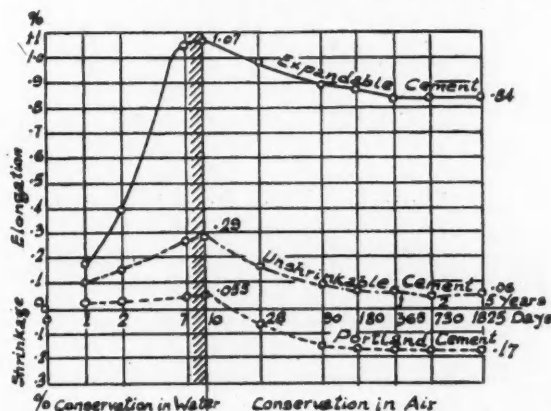


Fig. 2.—Expansion of Cement Cured in Water and Air.

A comparison between the expansion and contraction of test pieces of expanding cements, non-shrinking cement, and ordinary Portland cement are given in Figs. 1 and 2. The test pieces, which were kept under observation for five years, were cured in water for the whole of this period to obtain the data given in Fig. 1, except that the specimens of Portland cement were kept in air. The data in

Fig. 2 relates to specimens cured in water for the first ten days and subsequently kept in air. The expansion of the test pieces of expanding cement and non-shrinking cement cured under water became stabilised in about ten days, but the specimens kept in air after the first ten days exhibit a normal degree of shrinkage which in effect reduces the initial expansion.

Fig. 3 shows the variation of the compressive strength of cement mortars with age. The tests, which were also extended over five years, show that the average rate of gaining strength is lower for the special cements than for ordinary Portland cement in early ages, but this loss of strength is regained in the course of time, and it is claimed that both expanding and non-shrinking cements ultimately attain a higher strength than that of the Portland cement upon which they are based.

Among other physical properties, expanding cements are claimed to produce concrete of improved impermeability. These cements are, however, subject to

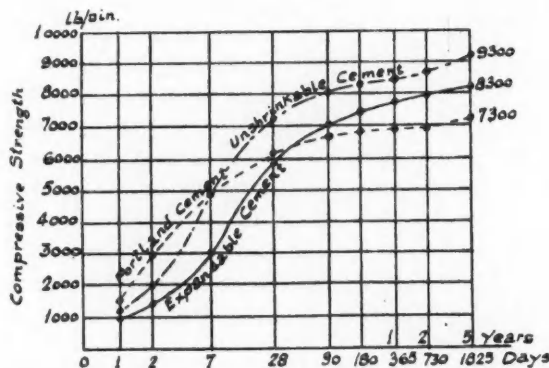


Fig. 3.—Compressive Strength of Mortars made with Expanding Cement.

deterioration during ordinary storage and, to offset this defect, expanding cement is usually supplied in bags in which a layer of paper coated with pitch is incorporated. Metal containers are used for deliveries in hot climates. These cements are also more susceptible to attack by sulphates and are therefore not suitable for marine construction or elsewhere where sulphates occur.

Applications of Expanding Cements.

Many practical applications of concrete made with expanding cements have been made in France. In the underpinning of structures such concretes have been found particularly useful. The piles or piers forming the new foundation are first constructed with their heads a few feet below the level of the bottom of the wall or other structure which it is intended to support. The intervening space is packed with expanding cement concrete. A number of holes, about 1 in. in diameter and spaced at intervals of about 8 ins., are formed in this concrete.

When the concrete has taken its initial set these holes are filled with water, the presence of which starts the expansion process. The latter, which is restricted by the position of the concrete between the old work and the new piers, continues for a few days until the calculated expansive force is attained, when the water is removed from the holes and within 24 to 48 hours the expansion ceases. The removal of the water constitutes a simple method of stopping the expansion during the execution of the work. The restricted expansive force ensures that the pressure between the old work and the new transfers the load of the former to the latter.

Another application is the use of expanding voussoirs in masonry and concrete arches, which are thereby put into a state of stress opposite in sense to the critical stresses induced by the loading of the structure and thus increasing the load-carrying capacity of the latter. This method has been adopted in repairing damaged bridges and a similar principle is employed in restoring damaged reinforced concrete structures. The members of the latter, due to their own weight, are in a state of stress (compressive stresses in the concrete are those principally concerned) and any new concrete placed in the breaches in these members should also be initially stressed if it is to strengthen the structure under dead load and contribute to the carrying of the superimposed loads. An expansive concrete filling, inserted in such a fashion that the partially restricted expansion induces a thrust against the old concrete, fulfils this object.

In addition to the foregoing it is considered that many other constructional problems might be solved by the use of expanding cements, and some of these are already in a trial stage.

A German Rapid-Hardening Cement.

A RAPID-HARDENING cement, termed "Schmelz," that has been developed in Germany is described in Report No. PB-22813 obtainable from the Office of Technical Services, Department of Commerce, Washington, D.C., United States (Price 1 dollar). The ingredients, which are melted before being finely ground, are calcium, aluminium, and ferrous and silicon oxides. The formula for the cement and a brief description of its manufacture are contained in the report, which was prepared by Lt.-Cdr. T. M. Prentice for the U.S. Naval Technical Mission in Europe. Also included in the report are the results of tests made for the German navy. These show that the cement is highly resistant to attack by sulphates and can be mixed with water containing as much as 250 milligrammes of carbon dioxide per litre without harmful results.

The cost of Schmelz cement is about three times that of Portland cement and it is therefore only economical when conditions require high initial strength and high resistance to chemical attack. It is stated that concrete made with this cement can be safely placed when the temperature is -7°C . The cement cannot be mixed with Portland cement because the heat generated during setting is so great that it decomposes Portland cement. The foregoing notes are taken from the Journal of the American Concrete Institute for September, 1946.

Phase Diagrams of Ternary Systems.

METHODS of interpreting phase diagrams in connection with industrial processes are discussed by Mr. L. A. Dahl in Bulletin No. 10 of the Research Laboratory of the Portland Cement Association, of Chicago, entitled "Interpretation of Phase Diagrams of Ternary Systems."

The author states that conventional interpretations of phase diagrams of systems of the refractory oxides describe the order of appearance and disappearance of solid phases when liquids of various compositions are cooled slowly. In applying phase equilibria data to problems pertaining to Portland cement manufacture, in which raw material mixtures are only partially fused, it has been found advantageous to follow a somewhat different mode of attack. Methods have been developed for determining the phases present at equilibrium at any given temperature, and estimating their proportions, without tracing the course of crystallization from the liquid state. In addition, attention has been given to the rôle of the liquid phase in the processes of fusion and crystallization as a means of gaining an understanding of the mechanism by which the oxides in the raw materials are transformed into the various cement compounds. These methods may be found useful in other fields, and are presented in the paper in a study of hypothetical ternary systems. The paper deals only with condensed systems in which the solid phases are practically immiscible.

In descriptions of the course of crystallization it is customary to assume an ideal condition, in which cooling is so slow that at each temperature a state of equilibrium is attained before a further reduction in temperature takes place. This condition may be described as a continuous attainment of equilibrium during the process of cooling. When there is a continuous attainment of equilibrium, the phase diagram supplies all the information necessary to predict the phases present at any stage in the process, and to estimate their proportions, by a process of deduction involving the mathematical properties of the triangular diagram.

With a slow attainment of equilibrium the process of cooling must be extremely slow if a continuous attainment of equilibrium is to be secured. The conclusions in regard to the course of crystallization obtained by assuming a continuous attainment of equilibrium consequently apply only to cases in which the process of cooling is so slow that this condition is secured. In an industrial process the condition must be known to exist before it can be assumed that the predicted changes in character and proportions of phases actually occur. It is not enough to know that a time element is involved in the process. It must be known that the rate of temperature change in the process is sufficiently slow to secure the continuous attainment of equilibrium. This cannot be known from the phase diagram, but can only be known by observations in addition to those represented in the diagram.

The paper is not confined to a study of changes occurring with a continuous attainment of equilibrium, but deals also with the changes which may occur if

temperature change is too rapid to permit such a condition to exist. Because of the fact that most discussions of the course of crystallization assume the continuous attainment of equilibrium, the author departs from conventional methods of presenting the subject and adopts a new method of treatment.

In discussing the rôle of the liquid phase in processes of fusion and crystallization, the author states that in dealing with systems in which the number of primary-phase regions is not greater than the number of components, the processes of fusion and crystallization may be treated as purely physical processes. When there are more primary-phase regions than the number of components, and the invariant points are eutectics, the course of crystallization, starting with the liquid state, may be treated as a physical process. However, in considering the process of fusion, complete or partial, the chemical changes occurring in the liquid phase must be recognized. In the case of systems in which there are non-eutectic invariant points, the fact that chemical changes occur in the course of crystallization is apparent.

In processes involving partial fusion of refractory materials the chemical reactions which produce the mineral constituents in the product occur in the liquid phase. For example, Portland cement raw mixtures are converted into the cement minerals very slowly at temperatures below that of liquid formation. When the temperature is raised to a point at which liquid appears, chemical changes occur rapidly. The liquid not only acts as a medium of rapid exchange for the various components, but its equilibrium relations with the various possible solid phases in the system determine the solid phases which will be formed.

Crystallization is treated as a physical process, with departures from this treatment only when the necessity arises because chemical change is evident and cannot be ignored. This mode of treatment is proper, since it is impossible to predict all of the possible applications of the phase equilibria data and the conditions under which departures from the ideal conditions may become important. On the other hand, application of the phase diagram to industrial problems may require consideration of the manner in which equilibrium is attained in the process of fusion, and also the effects of failure to attain equilibrium during fusion or crystallization. In such applications the rôle of the liquid phase must be taken into account.

International Cement Congress.

AN International Cement Congress was recently held in Stockholm, Sweden, and was attended by delegates from Belgium, Britain, Denmark, France, Holland, Norway, Sweden, and Yugoslavia. It was decided to establish a bureau entitled the "Cement Statistical and Technical Bureau" to serve as a medium for the exchange of information on technical and economic matters connected with the cement industry. The headquarters of the bureau will be in Norway.

The Study of Clay Minerals.

At a meeting on June 6 of the Council of the Mineralogical Society a proposal was considered for the formation within the Society of a group for the specialised study of the clay minerals, and the Council agreed in principle to the formation of such a group. A committee was appointed to frame the general conditions under which such groups might be established and operate.

An inaugural meeting of the Clay Minerals Group is to be held on January 24 at the premises of the Geological Society, Burlington House, Piccadilly, London, W.1, when it is hoped that representatives of various laboratories in Britain and abroad will give short reviews on present and projected research on clay minerals. Anyone interested is invited to attend, whether a member of the Society or not, and should apply to Mr. D. M. C. MacEwan, at Rothamsted Experimental Station, Harpenden, Herts, for details of the programme.

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